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Infrared E-type band profiles of acetonitrile in condensed media: Orientational diffusion and free rotation

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Abstract

Infrared spectra of liquid acetonitrile (CH3CN) and its solutions in CCl4, CS2, chloroform, dichloromethane, benzene-d6, acetone-d6 and dimethyl sulfoxide-d6 have been studied. E-type bands under investigation (ν5 = 3009, ν6 = 1448 and ν7 = 1041 cm-1) were reproduced by the sum of two Cauchy-Gauss components, the narrower (n) and the broader (b) ones. The different temperature behaviour of the components has been found: the integrated intensities of the narrower components, In, decrease with the temperature, while the intensities of the broader ones, Ib, increase. The narrower components of the bands were explained within the framework of the orientational diffusion mechanism. The broader components of ν6 and ν7 were attributed to the unresolved gas-like vibration-rotational absorption of the molecules. The enthalpy difference between the molecules absorbing via these two different mechanisms was determined from the dependence of ln(In/Ib) upon T-1:ΔH0 = 1.26±0.15 kcal mol-1. The broader component of ν5 is assumed to be mainly due to interactions of C-H stretching vibrations with single particle and collective motions of molecular dipoles. The narrower components' widths were used for evaluating the spinning diffusion constant of CH3CN. The absorption in C-H stretching region was found to be strongly affected by solvent. These effects were explained within the framework of hydrogen bond formation between the CH3-group of acetonitrile and H-bond acceptor groups of the solvent molecules.

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